FROM CARBON DIOXIDE TO C_2 ORGANIC MOLECULES

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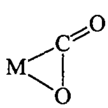
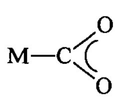
Abstract

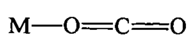
Research on the conversion of carbon dioxide into C_2 or higher organic molecules has received much attention in recent years. The key to the success of this research is carbon-carbon coupling. This paper reports the modified synthesis of a nickel carbon dioxide complex, $(Cy_3P)_2NiCO_2$, (Cy = cyclohexane) and the "Wittig Reaction" of this coordinated nickel carbon dioxide complex. The formed nickel ketene complex, $(Cy_3P)_2Ni[\eta^2\text{-}(C,O)\text{-}CH_2{=}C{=}O]$, has an unusual η^2-C,O bonding mode instead of the normal η^2-C,C for the later transition metals. The pathway of this "Witting Reaction" is an unprecedented example for a transition metal carbon dioxide complex.

Carbon dioxide chemistry has been a research topic for many research groups due to its fundamental importance and practical applications. To develop efficient catalytic processes in which carbon dioxide can be used as a carbon source is one of the main objectives of this research area.[1] Carbon-carbon coupling is the key to achieve C_2 or higher organic molecules. We are reporting the first example of "Wittig Reaction" on a coordinated carbon dioxide nickel complex.

Coordination of carbon dioxide to a transition metal is one of the initial steps in the catalytic conversion of carbon dioxide into useful organic molecules. The electronic structure of carbon dioxide is perturbed by bonding to a transition metal center. Different types and degrees of altered reactivities have been observed for different coordination modes of carbon dioxide. Two coordination modes for mononuclear metal carbon dioxide complexes have been reported[8]. They are η^2 side-on coordination and η^1-C coordination.

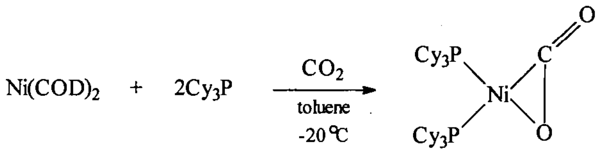

η^2-side-on coordination


η^1-C coordination


η^1-end-on coordination

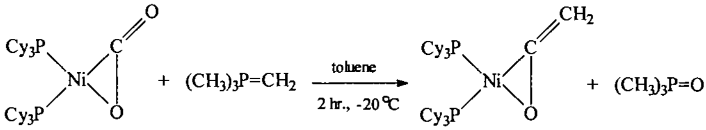
The η^2-side-on and η^1-C coordination modes are well established. The η^1 end-on coordination is a proposed mode as a result of calculation and has only been mentioned once as an intermediate in the literature[36]. Theoretical studies of these coordination modes of carbon dioxide have given a better understanding of the factors governing the bonding in carbon dioxide complexes. The η^2 side-on mode is preferred when the metal has a $d\pi$ orbital as the HOMO and the empty $d\sigma$ orbital pointing to the carbon dioxide ligand. One of the examples is Mo(0) in Cp_2MoCO_2, where Cp = cyclopentadiene. The η^1-C mode is most favored when the HOMO is mainly composed of a dσ orbital and when the metal is in a low oxidation state, as found in the d^8 complexes[17].

The η^2- coordinated nickel carbon dioxide complex, $(Cy_3P)_2NiCO_2$, is favored as a starting complex with the ylide due to the electrophilic carbon of the coordinated CO_2. The complex was first prepared by Michele Aresta in 1974[1a,4]. Based on the literature procedures, the preparation was modified to a one step procedure:



where COD is 1,5-cyclooctadiene. A 50 ml Schlenk reaction flask was charged with $Ni(COD)_2$, two equivalent of tricyclohexylphosphine and a minimum amount of anhydrous toluene in a nitrogen atmosphere dry box. The reaction flask was immediately brought out of the dry box and placed in an ice/salt cooling bath. bubbled the reaction solution with carbon dioxide gas via a syringe needle for about thirty minutes. During the above process, the product was precipitated out as yellow crystalline solid. The product was filtrated and washed with a small amount of ether in the dry box. The yield is around 85%. The spectral data are in agreement with the literature values. The C=O in coordinated CO_2 is characterized by a strong IR band at 1740 cm^{-1}. The $^{31}P\{^1H\}$ NMR of $(Cy_3P)_2NiCO_2$ in C_6D_6 shows a singlet at 37.32 ppm at 298 K. The $^{31}P\{^1H\}$ NMR of $(Cy_3P)_2NiCO_2$ in THF-d_8 at 188K shows two doublets $^2J_{p\text{-}p}$ = 39.6 Hz at 51.7 and 20.2 ppm, respectively[4]. The estimated value for the free activation temperature of the dynamic process at the coalescence temperature (233 K) is 39.3 KJ mol^{-1}.

Trialkyl phosphorus ylides, $R_3P{=}CH_2$, are strong nucleophiles. They react with organic ketenes and aldehydes to form alkenes via a [2+2] cycloaddition mechanism. Such ylides can also react with bridging carbonyls in $[\eta^5\text{-}CpFe(CO)_2]_2$ and $Ni_2(\mu\text{-}CO)(CO)_2(dppm)_2$, dppm = bis(diphenylphosphino) methane, to form μ-alkylidene complexes through the same C-C bondformation mechanism[5]. The carbon of η^2-CO_2 metal complexes has demonstrated some interesting reactivities towards nucleophiles[6]. The reaction between a metal CO_2 complex and an ylide is an unprecedented example in carbon dioxide chemistry. When $(Cy_3P)_2NiCO_2$ is treated with excess of trimethyl phosphorus ylide at room temperature in toluene, a nickel ketene complex is formed[7]:



Free organic ketenes are very reactive molecules. They can be stabilized by transition metal complexes. Transition metal ketene complexes are important intermediates in catalysis such as in the Fischer-Tropsch process. The process involves the catalytic CO activation and carbon-carbon coupling chemistry[8]. Ketenes can be bonded to transition metal complexes in a wide variety of ways[8a].

The two common bonding modes for mononuclear ketene complexes are η^2-(C, O) and η^2-(C, C). Traditionally, the η^2-(C, O) mode is considered to be favored by early transition metal complexes due to the electrophilic property of early transition metals. The η^2-(C, C) mode is preferred by late transition metal complexes. Several nickel ketene complexes have been reported and characterized spectroscopically to be the η^2-(C, C) bonding mode[8a]. The nickel ketene complex we obtained in the above reaction is characterized to be η^2-(C, O) bonded. A strong stretch at 1611 cm^{-1} is assigned to the C=C double bond. The first structure of an η^2-(C, O) bonded nickel ketene complex was reported recently by Hofmann's group[9]. The nickel diphenylketene complex, (dtbpm)Ni[η^2-(C, O)-Ph_2C_2O], has a strong band at 1643 cm^{-1} for the C=C double bond, where the chelated ligand, dtbpm, is Bis(di-tert-butylphosphino)methane.

Transition metal ketene complexes have demonstrated much interesting chemistry. The coordinated ketene can be readily converted to various organic molecules such as alcohols, aldehydes, acetones and acids[8]. The preliminary investigation shows that the nickel ketene complex we isolated has its own characteristic reactivity which is different from the η^2-(C, C) species, $(Ph_3P)_2$Ni[η^2-(C, C)-CH_2=CO], reported in the literature[10]. Our nickel ketene complex can react with HCl to generate acetaldehyde. Ligand effect studies are underway to understand the bonding modes of η^2-(C, C) and η^2-(C, O) to nickel complexes.

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7. The $^{31}P\{^{1}H\}$ NMR (CD_3CN, 85% H_3PO_4 external) for $(Cy_3P)_2Ni[\eta^2$-(C, O)-CH_2=CO]: singlet at δ 27.15 ppm, The coupled spectrum of the byproduct, Me_3P=O, shows a multiplet of ten peaks centered at δ 37.98 ppm due to the coupling of phosphine to the nine protons in Me_3. FTIR: 1611 (s) cm^{-1} for C=C, ^{1}H NMR for the CH_2 group of the coordinated ketene is at δ 2.45 (br) ppm, The yield is 52%.

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